BOLT TIGHTENING STRUCTURE OF MAGNESIUM ALLOY MEMBER

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a bolt tightening structure of a magnesium alloy members, and more particularly to a technology for preventing occurrence of electrolytic corrosion of the magnesium alloy member.

[0002] Recently, in the automobile industry, as the concern about environmental problems increases, a further improvement of fuel economy has been demanded. To meet such demand, in the automobile industry, it is required to reduce the weight of the car body, and magnesium alloys are widely used in automotive parts owing to their lightest weight among practical metals. More lately, in particular, they are applied in locations where very high corrosion resistance is required such as exterior and structural parts.

[0003] However, since the magnesium alloy is the basest practical alloy, when it is tightened with a heterogeneous metal such as iron or aluminum, electrolytic corrosion is likely to occur in the presence of moisture containing electrolyte. Especially for automobiles used outdoors, electrolytic corrosion is extremely promoted by the function of electrolyte contained in rainwater, seawater, or snow-melting salt, possibly causing breakage or damage of parts.

[0004] Japanese Laid-open Patent No. 5-302614 proposes a technology for preventing electrolytic corrosion by interposing a paper washer coated with resin between a magnesium alloy member and a steel bolt so as to avoid contact between the bolt and the magnesium alloy member. However, as the bolt corrodes, corrosion products flow out onto the magnesium alloy to cause electrolytic corrosion, and therefore it was impossible to apply in the position where corrosion resistance was required. It may be also considered to insulate between a bolt head and a magnesium alloy member by means of a resin washer, but the resin creeps by heat in coating, and the bolt shaft power lowers, and retightening is required, and hence it is not practicable. Moreover, recently, automakers in Europe have developed techniques for interposing an organic material containing inorganic fillers between a magnesium alloy member and a bolt. In such techniques, however, after 20 cycles of composite corrosion test by salt spray, occurrence of electrolytic corrosion was noted, and it was far from satisfaction of recent demands.

SUMMARY OF THE INVENTION

[0005] It is hence an object of the invention to provide a bolt tightening structure of a magnesium alloy member capable of insulating between a magnesium alloy member and a steel bolt without lowering the bolt shaft power, and preventing occurrence of electrolytic corrosion even in contact with electrolyte such as water.

[0006] The present invention is a bolt tightening structure of a magnesium alloy member for tightening magnesium alloy members with each other or a magnesium alloy member and a heterogeneous material by means of a bolt, wherein a cationic electrodeposition coating having a film thickness of 15 μm or more is provided at least on the surface of the magnesium alloy member contacting with a bolt head, a powder coating having a film thickness of 40 to 150 μm is provided on the surface of the cationic electrodeposition coating, zinc-nickel plating and then cosmer treatment are carried out on the bolt, and an alumite-treated aluminum washer is interposed between the bolt head and the magnesium alloy member.

[0007] As investigated by the present inventors, without cationic electrodeposition coating, even if a powder coating is applied in a sufficient thickness, the adhesion of the powder coating is poor, and local surface corrosion or electrolytic corrosion is likely to occur. In contrast, when a cationic electrodeposition coating is applied, the adhesion of the coating is sufficient, and such defect does not occur. However, when the film thickness of the cationic electrodeposition coating is less than 15 μm, corrosion resistance is extremely lowered, and hence the film thickness is preferably 15 μm or more. With the cationic electrodeposition coating only, the cationic electrodeposition coating film may be scratched by torque when tightening a bolt, and electrolytic corrosion is likely to grow from flaws. It is therefore essential to apply powder coating after cationic electrodeposition coating as proposed in the present invention. If the film thickness of the powder coating is less than 40 μm, the coating appearance

is extremely deteriorated and the film thickness is locally reduced to cause electrolytic corrosion easily. In contrast, if the film thickness is over 150 μm, the shaft power is lowered when tightening the bolt.

[0008] On the other hand, the bolt is treated by zinc-nickel plating and then cosmer process. Generally, for a bolt used in tightening of a magnesium alloy member, tin-zinc plating is preferable because the potential difference from magnesium is small. However, tin-zinc plating is not so superior in corrosion resistance, and the bolt corrode easily. When the bolt corrode, corrosion products flow to cause electrolytic corrosion between the corrosion products and magnesium alloy. The bolt treated by zinc plating and cosmer process is superior in corrosion resistance, and there is no problem in tin-zinc plating, and such bolt is easily available commercially.

[0009] As far as a bolt is made of steel, when used alone, potential difference from magnesium alloy cannot be eliminated completely. When tightening the bolt, moreover, due caution is needed not to scratch the coat surface by the bolt head. From such viewpoint, it is required to use an insulating washer in order to protect and insulate the magnesium alloy member. In this case, considering the insulation, corrosion resistance, and bolt shaft power, an alumite-treated washer are ideal. Alternatively, an iron or aluminum alloy washer treated by providing a cationic electrodeposition coating having a film thickness of 15 μm or more can also be used. In this case, if the film thickness of the cationic electrodeposition coating is less than 15 μm, current may locally pass, and

depending on the bolt tightening torque or number of times of repetition of tightening, there is a slightly possibility of occurring electrolytic corrosion on the magnesium alloy member.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Fig. 1 shows photographs of test pieces after salt spray test according to Examples 1 to 5 of the present invention.

[0011] Fig. 2 shows photographs of test pieces after salt spray test according to Examples 6 to 9 of the present invention.

[0012] Fig. 3 shows photographs of test pieces after salt spray test according to Comparative Examples 1 to 6.

[0013] Fig. 4 shows photographs of test pieces after salt spray test according to Comparative Examples 7 to 12.

[0014] Fig. 5 shows photographs of a wide range of test pieces after salt spray test according to Examples 1 and 4, and Comparative Example 8.

BEST MODE FOR CARRYING OUT THE INVENTION

[0015] Preferred embodiments of the present invention are described below.

[0016] 1. Magnesium alloy member

A magnesium alloy member preferably contains Al in an amount of 5% by weight or more. If the content of Al is less than 5% by weight, corrosion resistance of the magnesium alloy member is lowered, and corrosion resistance of coated surface decreases, and it is not suited to bolt

tightening. The surface of the magnesium alloy member is preferred to be treated by any one of chromic acid chrome treatment (chromate treatment), chromium phosphate treatment, and manganese phosphate treatment. Cr or Mn is contained in the surface of the magnesium alloy member by such treatment, and by the oxidation and reduction reaction of these elements (change of valence), oxidation reaction of magnesium is suppressed, so that electrolytic corrosion may be prevented effectively.

[0017] Powder coating applied on the surface of a cationic electrodeposition coating preferably contains epoxy resin and polyester resin as a principal component. Considering outdoor use, these resins are highest in light fastness and superior in corrosion resistance.

[0018] 2. Bolt

After zinc-nickel plating and before cosmer treatment, a bolt is preferred to be treated by chromate treatment. As a result, corrosion resistance of the bolt is further enhanced, and electrolytic corrosion of the magnesium alloy member by corrosion products can be effectively prevented. Cosmer treatment is generally a process for coating bolt surface with ethylene-acrylic acid copolymer resin dispersion added water dispersing silica, silane coupling agent, and water dispersing chromium compound.

[0019] 3. Washer

In order to prevent tearing of an alumite layer and assure insulation when tightening bolt, the thickness thereof is preferred to be 10 μm or more, and more preferably 30 μm or more. Further, by coating adhesive or

thermoplastic resin sealer on the bolt tightening area, infiltration of electrolyte is prevented and resistance to electrolytic corrosion is enhanced.

[0020] 4. Tightening part

In the present invention, material of part to be tightened with the magnesium alloy member is assumed mainly to be iron or aluminum alloy. Of such tightening part, at least the surface contacting with the magnesium alloy member is preferably treated by cationic electrodeposition coating. The film thickness thereof is preferred to be 15 μm or more. The reason is the same when applying cationic electrodeposition on the magnesium alloy member. When an iron part is treated by zinc plating or zinc-nickel plating prior to such coating, the corrosion resistance may be further enhanced.

EXAMPLES

[0021] <Examples>

In the following, the present invention is further explained in detail by referring to Examples.

[0022] 1. Preparation of test piece

In a plate material of magnesium alloy (AM60B or AZ91D) of 70 mm in width, 150 mm in height and 3 mm in thickness, 6 holes of 9 mm in diameter were formed, and burrs were removed sufficiently. Such magnesium alloy plate was prepared as a test piece of Examples 1 to 5, and was pretreated and coated as shown in Table 1. In chromate treatment, chromic acid chrome treatment solution (trade name: NH35, produced by

Norsk Hydro Co., Ltd.) was used and chrome loading was 0.5 g/m^2. In manganese phosphate treatment, Mag Plus treating solution (trade name), produced by Ebina Electric Co., Ltd., was used. In cationic electrodeposition coating, Power Top V50 (trade name) produced by Nippon Paint Co., Ltd., was used, and the film thickness was 25 μm or 15 μm. In powder coating, an epoxy/polyester paint (trade name: Powdux P60, produced by Nippon Paint Co., Ltd.) was used, and the film thickness thereof was 100 μm or 40 μm.

[0023] As a bolt, a steel flanged bolt of 8 mm in diameter, being treated by zinc-nickel plating, colored chromate treatment, and cosmer treatment (Strength 7T, produced by Ohashi Technica Co., Ltd.), was used. As a washer, a light alumite washer made of aluminum, being treated by sulfuric acid treatment and sealed by nickel acetate method (JIS A5182, produced by Ohashi Technica co., Ltd.), was used. The thickness of an alumite layer of the washer was set at 10 μm or 30 μm.

[0024] 2. Bolt tightening

As a tightening part, an iron plate in which screw holes suited to the bolt diameter were formed, zinc phosphate treatment was carried out and a cationic electrodeposition coating having a film thickness of 15 μm was provided, was used. A magnesium alloy test piece was put on the iron plate, and tightened by a bolt and a washer. The bolt was tightened by an air impact wrench to specified torque. Lowering of shaft power of the bolt after tightening was investigated. With respect to the bolt shaft power test, after tightening the bolt to specified torque, it was held at 100°C

for 60 minutes, and then the shaft power thereof was measured. In Table 1, the following criteria were used: cases where the measured value was lower than the initial shaft power by more than 20%: ×; and cases where it was within 20%: ○. When lowering of the shaft power is within 20%, retightening process can be omitted by setting the initial shaft power slightly higher.

[0025] 3. Salt spray test

The test pieces after bolt tightening were evaluated by salt spray test to investigate about swelling of the coat film and occurrence of electrolytic corrosion near a bolt tightening area in the magnesium alloy test piece. The results are shown in Table 1. In the salt spray test, 5% NaCl solution was sprayed to the test piece at a flow rate of 1.5 ml/min for 1200 hours. "Swelling of coat film" refers as a state in which the coat film near a bolt tightening area of a magnesium alloy member changes in appearance due to corrosion of the lower side thereof. "Electrolytic corrosion" refers as a state in which a large-scale pitting corrosion accompanied by peeling of a coat film occurs near a bolt tightening area. Further, it was investigated whether corrosion occurred at the edge of the test piece due to flow-out of corrosion products produced by corrosion of the bolt, and the results are also shown in Table 1.

Table 1

Ordinary torque tightening	Example 1	Example 2	Example 3	Example 4	Example 5
Magnesium alloy member					
Material	AM60B	AM60B	AM60B	AM60B	AZ91D
Chromate treatment	Treated		Treated	Treated	Treated
Manganese phosphate treatment		Treated			
Cationic electrodeposition coating (25 μm)	Treated	Treated		Treated	Treated
Cationic electrodeposition coating (15 μm)			Treated		
Powder coating (100 μm)	Treated	Treated		Treated	Treated
Powder coating (40 μm)			Treated		
Washer					
Alumite treatment (10 μm)	Treated	Treated	Treated		Treated
Alumite treatment (30 μm)				Treated	
Bolt					
ZnNi plating / Cosmer treatment	Treated	Treated	Treated	Treated	Treated
Salt spray test result					
Swelling of coat film in bolt tightening area	None	None	None	None	None
Electrolytic corrosion of material in bolt tightening area	None	None	None	None	None
Corrosion at material edge	None	None	None	None	None
Tightening performance					
Decrease of bolt shaft power	None	None	None	None	None
Overall evaluation	○	○	○	○	○

[0026] As shown in Table 1, in Examples 1 to 5, after bolt tightening, the shaft power was not lowered at all. Fig. 1 shows photographs of test pieces after salt spray test according to Examples 1 to 5. As shown in Table 1 and Fig. 1, in the magnesium alloy test pieces, swelling of coat film and electrolytic corrosion in the bolt tightening area did not occur at all,

and edge corrosion was not recognized.

[0027] 3. Bolt over-torque tightening and salt spray test

The same magnesium alloy plates as in Examples 1 to 5 were prepared as test pieces in Examples 6 to 9, and were pretreated and coated as shown in Table 2. The magnesium alloy test pieces were tightened to iron plates in the same manner as in the above Examples. At this time, the bolt was tightened to torque of 1.2 times that of the above Examples, and this over-torque tightening and loosening were repeated 10 times. After the same salt spray test, swelling of coat film near the bolt tightening area of the magnesium alloy test piece, presence or absence of electrolytic corrosion, and corrosion at the edge of the test piece were investigated. The results are also shown in Table 2.

Table 2

Over-torque tightening repeated 10 times	Example 6	Example 7	Example 8	Example 9
Magnesium alloy member				
Material	AM60B	AM60B	AM60B	AM60B
Chromate treatment	Treated	Treated	Treated	Treated
Cationic electrodeposition coating (25 μm)			Treated	
Cationic electrodeposition coating (15 μm)	Treated	Treated		Treated
Powder coating (100 μm)	Treated			
Powder coating (40 μm)		Treated	Treated	Treated
Washer				
Alumite treatment (10 μm)	Treated		Treated	Treated
Alumite treatment (30 μm)		Treated		
Bolt				
ZnNi plating/cosmer treatment	Treated	Treated	Treated	Treated
Salt spray test result				
Swelling of coat film in bolt tightening area	None	None	Present	Present
Electrolytic corrosion of material in bolt tightening area	None	None	None	None
Corrosion at material edge	None	None	None	None
Overall evaluation	◎	◎	○	○

[0028] Fig. 2 shows photographs of test pieces after salt spray test according to Examples 6 to 9. As shown in Table 2 and Fig. 2, in the magnesium alloy test pieces of Examples 6 and 7, swelling of coat film in bolt tightening area and electrolytic corrosion did not occur at all, and edge corrosion was not recognized. In contrast, in the magnesium alloy test pieces of Examples 8 and 9, swelling of coat film in bolt tightening area was recognized. It is estimated to be due to effects of a powder coating

having a thickness of 40 μm and an alumite layer of washer having a thickness of 10 μm.

[0029] Overall evaluations were carried out by the above results, and the evaluations are shown in Table 1 and Table 2. In the overall evaluation, the following criteria were used: cases where a problem occurred in any one of the items in bolt tightening at specified torque: ×; cases where no problem occurred at specified torque: ○; and cases where no problem occurred at over-torque: ◎. As a result, the result was ◎ in Examples 6 and 7, and ○ in all other Examples.

[0030] <Comparative Examples>

The same magnesium alloy plates as in the above Examples were prepared as test pieces of Comparative Examples 1 to 12. These test pieces were pretreated and coated as shown in Table 3 and Table 4. Using bolts and washers specified in Table 3 and Table 4, and the same iron plates as in the above Examples, the bolt was tightened to specified torque. Herein, "chelating treatment" shown in Table 3 and Table 4 is a kind of pretreatment for coating, and it refers as a treatment for chelating Mg component by treating a magnesium alloy plate with azole having a hydrazine structure. Other pretreatments and coating conditions were the same as in the above Examples.

Table 3

Ordinary torque tightening	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Magnesium alloy member						
Material	AM60B	AM60B	AM60B	AM60B	AM60B	AM60B
Chromate treatment	Treated	Treated		Treated	Treated	Treated
Chelating treatment			Treated			
Cationic electrodeposition coating (25 μm)	Treated			Treated	Treated	Treated
Powder coating (100 μm)		Treated	Treated	Treated	Treated	Treated
Powder coating (200 μm)						
Washer						
Alumite treatment (30 μm)	Treated	Treated	Treated		Treated	Treated
Iron				Iron Washer		
Resin						
Bolt						
ZnNi plating/cosmer treatment	Treated	Treated	Treated	Treated		
Dacro treatment					Treated	
Chrome plating						Treated
Zinc plating						
Tin-zinc plating						
Salt spray test result						
Swelling of coat film in bolt tightening area	Present	Present	Present	Present	None	None
Electrolytic corrosion of material in bolt tightening area	Present	Present	Present	None	None	None
Corrosion at material edge	None	None	None	None	Present	Present
Tightening performance						
Decrease of bolt shaft power	None	None	None	None	None	None
Overall evaluation	×	×	×	×	×	×

Table 4

Ordinary torque tightening	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12
Magnesium alloy member						
Material	AM60B	AM60B	AM60B	AM60B	AM60B	AM60B
Chromate treatment	Treated	Treated	Treated	Treated	Treated	Treated
Chelating treatment						
Cationic electrodeposition coating (25 μm)	Treated	Treated	Treated	Treated	Treated	
Powder coating (100 μm)	Treated	Treated		Treated	Treated	Treated
Powder coating (200 μm)			Treated			
Washer						
Alumite treatment (30 μm)	Treated	Treated	Treated			Treated
Iron						
Resin				Resin Washer		
Bolt						
ZnNi plating/cosmer treatment			Treated	Treated	Treated	
Dacro treatment						
Chrome plating						
Zinc plating	Treated					
Tin-zinc plating		Treated				Treated
Salt spray test result						
Swelling of coat film in bolt tightening area	None	None	None	None	Present	Present
Electrolytic corrosion of material in bolt tightening area	None	None	None	None	Present	Present
Corrosion at material edge	Present	Present	None	None	None	Present
Tightening performance						
Decrease of bolt shaft power	None	None	Present	Present	None	None
Overall evaluation	×	×	×	×	×	×

[0031] As a washer, an iron washer and a resin (plastic) washer were used, except for the almite washer having an alumite layer of 30 μm. As a bolt, bolts treated by Dacro treatment, chrome plating, zinc plating, and tin-zinc plating were used, except for the bolts used in the above Examples. "Dacro treatment" refers as a process treated by dacrotized treating solution (produced by Dacro Shamrock Japan Co., Ltd.).

[0032] With respect to these test pieces of Comparative Examples, after salt spray test was carried out in the same condition as that in Examples, swelling of coat film near the bolt tightening area of the magnesium alloy test piece, presence or absence of electrolytic corrosion, and corrosion at the edge of the test piece were investigated. The results are shown in Table 3 and Table 4, and photographs of test pieces after salt spray test are shown in Fig. 3 and Fig. 4. In the following, the Comparative Examples will be analyzed.

[0033] In Comparative Example 1 in which powder coating was not applied on the magnesium alloy plate and in Comparative Examples 2 and 3 in which no cationic electrodeposition coating was provided, swelling of coat film and electrolytic corrosion occurred near the bolt tightening area of the magnesium alloy plate. In Comparative Example 4 using an iron washer, swelling of coat film occurred near the bolt tightening area of the magnesium alloy plate. In Comparative Examples 5, 6, 7, and 8 using a bolt treated by Dacro treatment, chrome plating, zinc plating, and tin-zinc plating only, respectively, corrosion of the bolt was significant, and corrosion products flowed out to corrode at the edge of the test piece. Fig.

5 shows photographs of test pieces after salt spray test of Examples 1, 4 and Comparative Example 8, and a flow-out state of corrosion products and corrosion at the edge of the test piece were observed in Comparative Example 8.

[0034] In Comparative Example 9, since the film thickness of powder coating was 200 μm which exceeds the upper limit (150 μm) of the present invention, and in Comparative Example 10, since the resin washer was used, although there was no problem in the coat film, the bolt shaft powers were lowered. In Comparative Example 11, since no washer was used, swelling of coat film and electrolytic corrosion occurred near the bolt tightening area of the magnesium alloy plate. In Comparative Example 12, since no cationic electrodeposition coating was provided and a tin-zinc plated bolt was used, swelling of coat film and electrolytic corrosion occurred near the bolt tightening area of the magnesium alloy plate, and corrosion at the edge of the test piece due to corrosion products of the bolt was also detected.

[0035] Overall evaluations of Comparative Examples 1 to 12 were carried out by the above results and the results are shown in Table 3 and Table 4. In all Comparative Examples, since there were problems when the bolt was tightened to specified torque, the overall evaluations were ×.